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ALUMINUM NITRIDE CRYSTAL GROWTH

G.A. Slack

FINAL REPORT

Contract F49620-78-C-0021

Period Covered

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## SUMMARY OF RESULTS

1. Devised a motor-driven syringe system for molten Al using hot-pressed AlN ceramic as the container walls and piston. This syringe produces small droplets of pure molten Al at a controlled rate for subsequent AlN synthesis.
2. Produce AlN by reacting the syringe droplets with  $\text{NH}_3$  gas at  $1750^\circ\text{C}$  to  $1850^\circ\text{C}$ .
3. Studied the sublimation rate and growth rate of AlN in  $\text{N}_2$  gas and cracked  $\text{NH}_3$  gas at high temperatures.
4. Devised a theoretical model to predict the measured sublimation rates.
5. Demonstrated that the optimum atmosphere for growing AlN crystals may be cracked  $\text{NH}_3$  gas at pressures of 10 to 100 atmospheres.
6. Prepared a single crystal of AlN inside a single crystal tungsten crucible in an atmosphere of cracked  $\text{NH}_3$ .
7. Proposed a new scheme for making AlN starting material from aluminum metal-organics.
8. Measured the thermal conductivity of AlN from  $100^\circ\text{K}$  to  $1800^\circ\text{K}$ , and showed that the behavior is intrinsic.

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## GENERAL ABSTRACT

From November 1, 1975 to October 31, 1977, Signal Electronics Laboratory personnel worked on the problem of Aluminum Nitride Heat Sink Crystal Growth for the U.S. Air Force Office of Scientific Research under Contract Number F44620-76-C-0039. From November 1, 1977 to the present we have worked on Aluminum Nitride and Boron Phosphide Crystal Growth under Contract Number F49620-78-C-0021. The present report covers the progress made from November 1, 1978 to October 31, 1979 on the crystal growth of aluminum nitride.

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## Section 1

### INTRODUCTION

Single crystals of aluminum nitride are potentially useful as electrically insulating heat sink substrates for semiconductor devices and as the active material for surface-acoustic-wave (SAW) devices. In the pure, undoped state it is a good electrical insulator and a good thermal conductor. It also possesses a good thermal expansion match to other active semiconductors. It shares these combined desirable properties with diamond and cubic boron nitride, but does not have to be made under high pressure. Thus, it is an attractive heat sink material. One of the standard heat sink materials at present is BeO. The thermal conductivity of AlN is comparable to that of beryllium oxide, but it has about one-half the thermal expansion coefficient of BeO, and is nontoxic. Hence, it is to be preferred over BeO. For SAW devices thin films of AlN have been used for about 15 years. The high piezoelectric coupling coefficient and the high acoustic velocity are very attractive for devices. However, no piezoelectric or elastic data exist on single crystals of AlN, and no single-crystal devices have been made. The devices are all based on thin films of AlN deposited on other substrates, such as  $\text{Al}_2\text{O}_3$ .

The growth of high-purity single crystals of AlN has been pursued recently by Slack and McNelly<sup>(8,9)</sup>, who have used metal crucibles to grow AlN by sublimation and recondensation. Growth from molten  $\text{Ca}_3\text{N}_2$  has been reported by Dugger at Air Force Cambridge Research Laboratories. Armington *et al.* have grown a few small crystals by sublimation in graphite crucibles at A.F.C.R.L. In Japan some small AlN crystals have been grown by using liquid iron as a solvent by a V-L-S method, and some have been grown by sublimation. The largest crystals, by far, are those grown by Slack and McNelly, where crystal sizes of 3 cm have been produced.

## Section 2

## PROGRESS DURING THE CURRENT YEAR

## I. Preparation of Starting Material

## A. Surface Wetting

The best way found in previous studies to make chemically pure AlN with a low oxygen content was to react Al metal with  $N_2$  gas. In an attempt to improve this process the  $N_2$  gas has been replaced by  $NH_3$  gas, and this has been reacted with drops of liquid aluminum. For this process we have studied possible containers for liquid aluminum, whose melting point is  $660^\circ C$  and boiling point is  $2494^\circ C$ . The candidates that have been tried are fused quartz, aluminum oxide, graphite, hot pressed boron nitride, pyrolytic boron nitride, and hot pressed aluminum nitride. The reaction of molten Al with fused quartz is too severe, and the containers were destroyed. The reaction at  $800^\circ C$  of molten aluminum with graphite is slight, but some aluminum carbide is produced. There is some reaction with  $Al_2O_3$  also, especially at high temperatures. Molten Al also reacts with BN to form AlN and B doped Al. The best container material is AlN ceramic<sup>(1,2)</sup>, and there is no reaction of it with Al metal. Hot-pressed AlN ceramic was purchased<sup>(3)</sup> with a density of 90% to 95% of theoretical and an oxygen content of about 3 weight percent. This material was used to fabricate parts by various grinding and sawing techniques.

The wetting behavior of molten Al metal on AlN ceramic has been studied during this present program in order to determine how the system behaves in  $NH_3$  gas. We have found that in  $NH_3$  gas molten Al can be contained in  $Al_2O_3$ , BN, or AlN containers at  $1000^\circ C$ . However, above  $1200^\circ C$  the molten Al creeps readily up the walls of the container, down the outside walls, and completely coats the crucibles with a thin layer of liquid Al. This effect has been studied by Rhee<sup>(4)</sup>, who found in sessile drop experiments that the contact angle between Al and AlN is  $90^\circ$  at  $857^\circ C$  and reaches  $180^\circ$  at  $1077^\circ C$ . Thus for all temperatures

above 1077°C molten Al will completely spread out to cover any AlN surface. This means that, in an atmosphere of  $\text{NH}_3$  where the spreading Al metal film is rapidly converted to AlN, the molten Al will coat any and all kinds of surfaces it contacts. This "superfluid" style of behavior has been seen in our present experiments with AlN, BN,  $\text{Al}_2\text{O}_3$ , and tungsten surfaces. It was reported previously for molten Al in BN crucibles in vacuum<sup>(5)</sup>, and for molten Ga on several surfaces in an  $\text{NH}_3$  atmosphere<sup>(6)</sup>.

The behavior of molten Al on  $\text{Al}_2\text{O}_3$  in vacuum has been studied by Brennan and Pask<sup>(7)</sup> who found that this system does not show complete wetting until the temperature reaches approximately 1800°C. Thus Al spreads on AlN at a much lower temperature than it does on  $\text{Al}_2\text{O}_3$ .

These results show that if we want to contain molten Al in an AlN crucible in an  $\text{NH}_3$  atmosphere, we need to stay at temperatures between 660°C and 1077°C. If we wish to react Al with  $\text{NH}_3$  to form AlN we should be at a temperature above 1077°C and below the stoichiometric sublimation temperature (1 atmosphere) of 2433°C. Above 1077°C the molten Al will creep over any AlN surface and make the reaction of Al and N proceed more rapidly.

#### B. Design of Molten Aluminum Syringe

The pellet-drop technique for making AlN has been published<sup>(9)</sup>. In this method solid Al pellets were made by machining, and were dropped, one at a time, into a hot reactor. The pellets were rather massive at 70 milligrams each, and the reaction with the nitrogen was not complete. The present idea is to eject small, spherical droplets of molten Al sequentially from a syringe at a constant rate. The syringe setup is shown in Figure 1. The body and piston are made from hot-pressed<sup>(3)</sup> AlN. The whole assembly is heated to about 800°C by the nichrome heater run at 160 volts, 60 hertz, at a power level of about 1200 watts.

The piston is driven continuously at a slow rate of about 2mm/hour. The droplets of Al emerge from a hole in the tip; the

hole diameter is 0.38mm. The droplet size is approximately 1.4mm diam, and each drop weighs about 3.9 milligrams. They fall at a rate of one droplet every 6 seconds. Occasionally, drops as large as 6mm diam. (320 milligrams) form on the tip of the syringe before falling. These large drops generally do not completely convert to AlN whereas the small droplets do. The reason for the formation of the large drops is not completely understood. This instability of drop size is a major unsolved problem.

The Al droplets fall into a heated, pyrolytic boron nitride crucible positioned 7 cm below the syringe. The BN crucible is held inside a tungsten susceptor which is heated by a radio frequency induction coil, see Figure 2. The crucible temperature is 1750°C, and the surrounding atmosphere is decomposed, high purity  $\text{NH}_3$  gas. The syringe and the hot crucible are both contained inside a bell-jar furnace.

The AlN made by this process is a dark, polycrystalline mass composed of small but visible crystallites of AlN with some excess Al sometimes trapped between the grains. The AlN grain size averages about 0.1mm with grains both 3 times larger and 3 times smaller than this. One small Al droplet of 1.4mm diam. thus makes about 3000 grains of AlN. This means it breaks up and nitrides at many different points on the surface. The residual Al metal remaining after nitriding is a few percent or less for these small droplets. For the larger drops over 3mm in diameter the nitridation is less complete, and as much as 10% to 20% of the Al may remain unreacted. In the previous<sup>(9)</sup> pellet-drop experiment the pellet mass was about 70 milligrams, and the nitridation was also incomplete. The present scheme works better under some conditions.

The results of the syringe droplet Al run in a mixture of  $0.95\text{N}_2 + 0.05\text{H}_2$  at 1 atmosphere pressure and 1820°C are shown in Figure 3 for run W252 at a magnification of 4.7 times (Neg. No. 49324AlA). The successive layer structure can be seen, particularly near the top where the droplet diameter was about 6mm and they fell every 150 sec. The dense, pore-free nature of the deposit is

apparent. The white, outside layer near the bottom is the boron nitride crucible. Figure 4 shows the results in one atmosphere of  $0.25\text{N}_2 + 0.75\text{H}_2$ , run W250, at a magnification of 7.0 times (Neg. No. 49324B1A). In these runs the drops were variable in size. The rod-shaped column in Figure 4 was formed mostly from 3mm diameter drops. The rapid reaction with the cracked  $\text{NH}_3$  prevents the flow-out of the liquid aluminum and a porous, more crystalline mass results. The porosity, however, exposes more surface to oxidation and some free aluminum is still present. The material made in Figure 3 is more easily handled and is to be preferred. However, a secondary reaction with nitrogen must be carried out with the product from either Figure 3 or Figure 4.

#### C. Secondary Reaction

In order to produce nearly stoichiometric AlN for the crystal growth it is still necessary to carry out a second nitridation step similar to that in Figure 3 of Ref. 9. Here the Al and AlN are sublimed and condensed in an all-tungsten apparatus. The deposit is a light-yellow to brownish-orange color instead of the grey to black color produced after the droplet run.



## II. Growth of AlN

### A. Sublimation Rate in $N_2$ and Cracked $NH_3$

A number of experiments have been conducted to measure the net evaporation rate of AlN inside of a tungsten crucible. For these experiments 7.5cm long, 1.3cm bore, chemically vapor deposited tungsten crucibles with a 0.6mm wall were used. These had a flat bottom and were fitted with a flat-topped cap which was welded, after adding the AlN grains, by an electron beam welder. The bottom of the crucible was placed in the center of an r.f. coil and the top protruded slightly from the coil. The top was thus 150°C to 300°C cooler than the bottom. After 1 to 10 hours of running time part of the AlN had condensed as a smooth layer on the inside top of the crucible. This AlN was removed by etching away the tungsten and then weighed. The rate of AlN buildup in millimeters of thickness per hour was calculated and is shown plotted in Figure 5.

The atmosphere surrounding the tungsten crucible was varied. For runs W16, W19, W20, W23, W25, W29, and W34 it was pure  $N_2$  at 1 atmosphere, or sometimes  $N_2 + 3\% H_2$ . For runs W235, W247 and W255 it was cracked ammonia with a composition of  $1N_2 + 3H_2$  at a total pressure of 1 atmosphere. For runs W16 through W34 the crucibles were welded shut, and the internal  $N_2$  pressure built up to 1 atmosphere by diffusion of N atoms through the tungsten walls. For runs W235, W247, and W255 a small leak was created through the walls so that the  $H_2$  and  $N_2$  inside and outside were in equilibrium. This is needed since the Al coating on the inside walls of the W crucible appears to prevent the inward permeation of hydrogen. In run W241 no hydrogen leak was provided, and the sublimation rate with cracked  $NH_3$  at 1 atmosphere pressure on the outside is anomalously low.

The measured transport rates in the crucibles are actually net rates because there is always some re-evaporation from the cold end of the crucible to the hot end. This has been corrected

for so that the data points in Figure 5 are the sublimation rate from a hot surface at the stated temperature toward a sink at absolute zero.

In Figure 5 there are also some calculated curves for the expected sublimation rate under various conditions. The agreement between experiment and theory for 1 atmosphere  $N_2$  or  $1N_2 + 3H_2$  is fairly good. From these calculated sublimation curves one can calculate the net growth rate of AlN inside a crucible as a function of the temperature difference between the hot and cold ends. These results are shown in Figure 6 for a hot end temperature of  $2400^\circ C$  at  $\Delta T = 200^\circ C$ , which is a  $\Delta T$  that produces good quality crystals, the growth rates are 0.5mm/hour, 0.9mm/hour and 13mm/hour for  $N_2$  at 1 atmosphere,  $3H_2 + 1N_2$  at 1 atmosphere, and  $3H_2 + 1N_2$  at 10 atmospheres. The growth rates measured at 1 atmosphere are in reasonable agreement with these predictions. The growth rate and/or sublimation rate at 10 atmospheres has not yet been measured. The substantial predicted increase places these measurements on the agenda of what to do next.

#### B. Theoretical Model for Sublimation Rate Calculations

The solid and dashed curves in Figure 6 were calculated from a model similar to that used in the interim report<sup>(10)</sup>. In this model the growing (or receding) surface is assumed to be covered with a layer of liquid Al metal and AlN is formed with unit probability whenever a monatomic nitrogen atom, N, strikes this Al surface. Henceforth we will talk about growth instead of sublimation since the two are equivalent. It is also assumed that  $N_2$  molecules are never captured when they strike the surface because their dissociation energy is too large, see Table I. The concentration of N atoms in the gas phase was calculated from the thermodynamic data in the JANAF tables<sup>(11)</sup>. The curve in Figure 5 labelled "stoichiometric" is that calculated from the  $N_2$  and N pressure over AlN when the vapor over AlN is that produced by congruent sublimation<sup>(8)</sup>. If the  $N_2$  is increased to 1 atmosphere, then for  $t < 2600^\circ C$  the growth rate is increased. This is the second curve in Figure 5. If the gas composition is

now changed to that of cracked  $\text{NH}_3$ , at the same pressure, the growth rate increases. In this case the concentration of N atoms drops below that for pure  $\text{N}_2$  at 1 atmosphere. However, there are also molecules of  $\text{NH}$ ,  $\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$  at low concentrations in the gas<sup>(12)</sup>, at concentrations similar to that of the N atoms. If some of these can be captured by the film of liquid Al, then the growth rate can be enhanced. The question is one of the magnitudes of the dissociation energies.

The dissociation energies<sup>(11)</sup> at 0°K for the various molecules are given in Table I. The values<sup>(11)</sup> at temperatures up to 3000°K are not significantly different. The energy released by forming one molecule of AlN (solid) from Al (solid) + N (gas) as:



is 8.12 ev. When N atoms are added to a liquid Al surface, 1/2 of the bonds in the crystal are formed, and the energy released is 4.06 ev. This energy is sufficient to dissociate  $\text{NH}$  and  $\text{NH}_2$  but not  $\text{NH}_3$ , see Table I. Thus N,  $\text{NH}$ , and  $\text{NH}_2$  molecules but not  $\text{NH}_3$  can be used to grow AlN crystals. The growth rates in Fig. 5 have been calculated by assuming that these molecules ( $\text{NH}$  and  $\text{NH}_2$ ) and N atoms are all captured with unit probability whenever they strike the surface. Their surface impact rate has been calculated from their partial pressures and rms velocities. For example the growth rate of AlN for the  $\text{NH}_2$  contribution is given by:

$$r(\text{NH}_2) = 6.896 \times 10^5 P(\text{NH}_2) \left[ \frac{1000}{T} \right]^{1/2} \text{ mm/hr.}$$

where  $P(\text{NH}_2)$  is the partial pressure in atmospheres and T is the absolute temperature in °K. At 2400°C and a total pressure of 1 atmosphere in cracked  $\text{NH}_3$  the relative contributions of  $\text{NH}_2$ ,  $\text{NH}$ , and N to the growth rate are: 47%, 33%, and 20%. At 10 atmospheres total pressure in cracked  $\text{NH}_3$  these change to 79%, 18%, and 3%. Thus the  $\text{NH}_2$  becomes dominant at higher pressures. The concentration of  $\text{NH}_2$  in cracked  $\text{NH}_3$  at fixed temperature increases as  $(P_{\text{TOT}})^{1.5}$  whereas the concentration of N increases

as  $(P_{TOT})^{0.5}$ . The conclusion is that hydrogen can really increase the growth rate of AlN crystals from the vapor phase, and some new experiments to test this model conjecture are needed.

If one could operate at  $P_{TOT} = 100$  atmospheres in cracked  $NH_3$  at  $2400^\circ C$ , the maximum growth rate would be about 750mm/hour or 12.5cm/minute. Even at this rate there would still be an overabundance of liquid Al on the crystal surface. The rate is not limited by the Al arrival rate until growth rates of  $10^5$  mm/hour are reached.

Note that the need<sup>(10)</sup> for single crystal tungsten crucibles for growing AlN is mandated by the long growing times needed in pure  $N_2$ . If the growth rate from the vapor phase can be increased substantially above 0.5mm/hour, then it may be possible to use the much cheaper polycrystalline tungsten crucibles for growing AlN. This would be an important improvement.

#### C. AlN Growth in a Single Crystal Tungsten Crucible

In the last interim report<sup>(10)</sup> the advantages of single crystal crucibles of tungsten for growing AlN were described. The main advantage is that the Al penetration of the walls is much less severe, and hence the crucible lifetime is about 88 times greater than for the polycrystalline tungsten. In an effort to test this scheme a large single crystal of pure tungsten was obtained from a commercial crystal grower<sup>(13)</sup>, and was fashioned into a tapered-end crucible. The crystal was 7.5cm long, 1.2cm in diameter and its main growth axis was  $30^\circ$  off the [100] direction. It was grown from the melt by an electron-beam, floating zone technique<sup>(14,15)</sup>. This crystal was fashioned into a crucible by grinding off the outer surface to form a circular cylinder 1.09 cm in diameter and 7.1 cm long, see Figure 7. The end of the original boule was removed and fashioned into a cap for the end of the crucible. The crucible was hollowed out by electrical discharge machining using copper-tungsten electrodes.

The endcap was welded to the end of the crucible with an electron beam welder, and was so oriented that the weld region regrows as a single crystal, see Figure 8.

The interior of the crucible is fitted with a conically pointed rhenium liner and the AlN charge is placed inside before welding. The controlled gas leak in the end cap is a 0.40 mm diam. tungsten wire fitted through a 0.41 mm diameter hole. This leak is designed to let  $H_2$  gas into the crucible in order to improve the growth rate. It is small enough so that the AlN mass loss during the growing time of, say, 100 hours will be about 0.01%. The rhenium liner is 0.1 mm thick. It is designed to be etched away by hot nitric acid at the end of the run. This acid attacks Re but not W or AlN. Thus, in theory crystal can be removed at the end of the run without destroying the crucible, as has been the custom heretofore. Another advantage of the rhenium liner is that its coefficient of thermal expansion is slightly larger than that of AlN. The AlN crystal is then under compression during cooling from the growth run. Thus it will not crack as readily as when it is in contact with tungsten. With tungsten it is under tension during cooling.

The difficulty with the rhenium liner scheme in practice is that during the long run at high temperatures it alloys with the tungsten crucible by solid-state diffusion. It was found impossible to remove it by etching. In order to remove the crystal from the crucible it was found necessary to etch away the whole single crystal crucible at the end of the run. This makes the single crystal crucible technique very expensive and suggests that polycrystalline tungsten crucibles under high pressure with added  $H_2$  to increase the growth rate is a better idea.

One growth run, W253, was made to test the single-crystal crucible method. The crystal from this run is shown in side view in Figure 9 at a magnification of 8 times (Neg. No. 49495A1A). It is 17mm long, 9mm in diameter at the large end and weighs 1.5 gm.

The scale at the bottom of the picture is in millimeters. It required 74 hours for the run at a hot end temperature of 2308°C and a push rate of 0.5mm/hr. A top view of the same crystal is shown in Figure 10 at a magnification of 10.5 times (Neg. No. 49495A1B).

#### D. Aluminum Reaction with Tungsten

The aluminum vapor from the AlN inside the tungsten crucible reacts with the crucible itself to some extent. It was found that the Al actually diffuses into the single crystal tungsten at high temperatures<sup>(10)</sup>. The diffusion coefficient measured<sup>(10)</sup> at 2385°C was  $D = 2.50 \times 10^{-10}$  cm<sup>2</sup>/sec. This low value of D is indicative of substitutional diffusion of Al, which moves from one tungsten lattice vacancy to another. The effect of Al on the lattice constant of tungsten at room temperature has been measured. The Al shrinks the x-ray lattice constant of tungsten, which is to be expected since the Al radius is smaller than that of W. The present measurements show that pure tungsten has

$$a_0 = 3.1647 \pm 0.0001 \text{ \AA}$$

while tungsten doped with  $5.4 \pm 0.1$  atom % aluminum has

$$a_0 = 3.1617 \pm 0.0005 \text{ \AA}$$

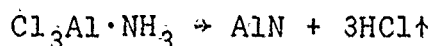
Thus  $\frac{\Delta a}{a_0 C} = -(1.8 \pm 0.4) \times 10^{-2}$ , where

C is the Al concentration. The Al was diffused into a 0.025 mm thick sheet of tungsten foil from an AlN source held inside a sealed tungsten crucible at 2330°C for 26 hours. This time is

sufficiently long so that the Al concentration throughout the foil is very nearly uniform. The Al concentration was determined with an electron beam microprobe apparatus using pure Al as a standard. The lattice contraction is indicative of a substitutional impurity. The interstitial impurities C and Si both appear to expand<sup>(16,17)</sup> the lattice of tungsten.

### III. Alternative Method of Preparing AlN

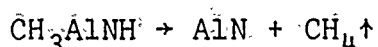
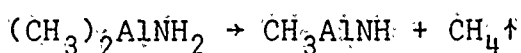
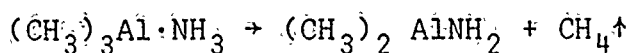
The liquid-droplet method of making AlN is time consuming, involves expensive equipment, and (as yet) does not yield reproducible droplet sizes. Thus some excess aluminum is trapped between the AlN grains. The alternative method of reacting  $\text{AlF}_3$  with  $\text{NH}_3$  gas has been tried previously, and described<sup>(8)</sup>. A literature survey of a third method using aluminum metal-organics was carried out. The forerunner of this method was the thermal decomposition of the adduct  $\text{Cl}_3\text{Al}\cdot\text{NH}_3$  on hot substrates at  $1000^\circ\text{C}$  to  $1500^\circ\text{C}$  which yields<sup>(18,19)</sup> a polycrystalline deposit of AlN plus HCl gas. The reaction is:



Several people (20-23) have made thin films of Al by the reaction of trialkyl aluminum with  $\text{NH}_3$  on a hot substrate at  $1200^\circ\text{C}$ .

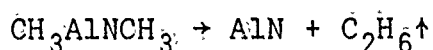
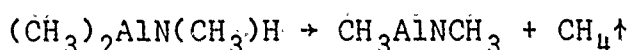
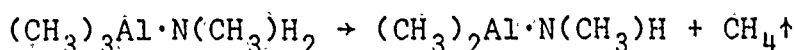
It would be most convenient to be able to produce AlN powder or ceramic by the in-situ thermal decomposition of a Lewis acid-Lewis base adduct of the type  $\text{R}_3\text{Al}\cdot\text{NR}'_3$ . The requirement is that the R-Al bonds and the N-R' bonds break up thermally at a low temperature before the Al-N bonds break and before the sample vaporizes. This was done by Wilberg, et al.<sup>(24,25)</sup> using  $\text{R}=\text{CH}_3$ =methyl and  $\text{R}'=\text{H}$ =hydrogen. The trimethyl aluminum and ammonia are reacted at a low temperature, to form  $(\text{CH}_3)_3\text{Al}\cdot\text{NH}_3$ . This adduct reaction can be carried out either in a solvent such as benzene, toluene, or cyclohexane.

Upon warming the solvent evaporates and the adduct decomposes in steps:



The first step is complete at about 70°C, the final step requires about 200°C for several hours. It appears possible<sup>(26)</sup> to use triethyl aluminum for this reaction as well, where  $\text{C}_2\text{H}_5$  = ethyl. The gaseous decomposition product is then ethane,  $\text{C}_2\text{H}_6$ .

Another possible variant of the above reactions is to use monomethyl or monoethylamine,  $\text{CH}_3\text{NH}_2$  or  $\text{C}_2\text{H}_5\text{NH}_2$  instead of  $\text{NH}_3$ . It might even be possible to use dimethyl or diethyl amines,  $(\text{CH}_3)_2\text{NH}$  or  $(\text{C}_2\text{H}_5)_2\text{NH}$ . For the monoethylamine the three reaction steps would be:



The first two steps have been carried out for triethyl and trimethyl aluminum by Gosling et al.<sup>(27)</sup> The thermal decomposition of  $\text{C}_2\text{H}_5\text{AlNCH}_3$ , ethyl aluminum-methyl amide, has not been studied by anyone to date. Whether it will decompose to  $\text{AlN} + \text{C}_3\text{H}_8$  remains to be seen. Perhaps some  $\text{Al}_4\text{C}_3$  may be produced if the Al-C bonds do not all break at low temperature. For example,  $\text{CH}_3\text{AlNCH}_3$  sublimes slowly in vacuum at 180°C without decomposition<sup>(28)</sup>. If one<sup>(29)</sup> uses dialkyl amine, then the decomposition has to deal with  $\text{R}_2\text{AlNR}'$ , where  $\text{R}'$  is an alkyl group and not hydrogen. Such complexes may be even more difficult to decompose<sup>(30)</sup> to  $\text{AlN}$  than the  $\text{RAlNR}'$  ones. New experiments are



needed to find out. For example, the compound methyl aluminum-methyl amide exhibits a cage structure<sup>(31)</sup> and is polymerized 7 times to give  $[\text{CH}_3\text{AlNCH}_3]_7$ . This is stable to at least  $210^\circ\text{C}$ . Whether this readily decomposes to  $\text{AlN} + \text{C}_2\text{H}_6$  (ethane) is unknown. Perhaps excess  $\text{H}_2$  gas would aid the decomposition into  $\text{AlN} + 2\text{CH}_4$ . Laubengayer<sup>(32)</sup> seems to think that only  $\text{R}_3\text{Al}\cdot\text{NH}_3$  adducts have sufficient hydrogen in the structure to decompose all the way to  $\text{AlN}$ . When the hydrogen on the nitrogen is replaced by a hydrocarbon group, he thinks that the thermal stability becomes too great to make only  $\text{AlN}$  during decomposition.

Various other adducts have been tried where either hydrogen or chlorine is attached to the aluminum ions<sup>(25,26,33-36)</sup>. These do not decompose to  $\text{AlN}$ . The aluminum hydride or dialkyl and monoalkyl alane adducts thermally decompose to yield free aluminum, while the chlorides retain the chlorine up to very high temperatures. Both of these should be avoided.

In order to make high purity  $\text{AlN}$  free of  $\text{Al}_2\text{O}_3$ , it is necessary to exclude all oxygen and water vapor from the reaction systems. Both trimethyl and triethyl aluminum react vigorously and spontaneously with  $\text{H}_2\text{O}$  or  $\text{O}_2$ . Trace amounts of oxygen in the system or starting materials will give rise<sup>(37)</sup> to  $\text{R}_2\text{AlOAlR}_2$ , tetraalkylaluminumoxane, or perhaps  $\text{R}_2\text{AlOR}$ , dialkyl aluminum alkoxide. These will probably not react with  $\text{NH}_3$  or  $\text{NR}_2\text{H}$  to form adducts. Rather they will probably thermally decompose upon heating to yield the solids  $\text{Al}_2\text{O}_3$  and  $\text{Al}_4\text{C}_3$ , and various volatile hydrocarbons. Some care will have to be exercised to separate these contaminants from the starting trimethyl or triethyl aluminum before they are used. The  $\text{NH}_3$  can be easily gettered of  $\text{H}_2\text{O}$  by using Na or K metal. Methods for cleaning up the aluminum compounds are unclear.

The starting materials for these reactions are relatively cheap. The triethyl aluminum is available from Ethyl Corporation<sup>(38)</sup> in tank-car lots at \$1.63/lb, equivalent to \$6.88 per pound of aluminum. Trimethyl aluminum is available from the same source in smaller lots at \$19/lb, equivalent to \$50.67/lb of aluminum metal. The nitrogen is even cheaper per pound as ammonia or alkylamines.

The big advantage of using the metalorganic adducts is that the Al and N are combined with each other on an atomic scale in a one-to-one ratio. Thus excess aluminum is not apt to be a contaminant in the resultant product unless there is some contamination with things like dialkyl alanes,  $R_2HAl$ . Free aluminum is a common contaminant from the direct reaction of Al metal with  $NH_3$  or  $N_2$ .

Thus metal organics may be a useful way to produce AlN. The advantages are maintenance of exact stoichiometry and of intimate mixing of the initial reactant atoms. The problem of maintaining purity in the range of 1000 ppm or less may be troublesome. For convenience a collection of melting points and boiling points of various compounds is given in Table II.

#### IV. Properties of Aluminum Nitride

##### A. Thermal Conductivity

One of the useful properties of AlN is its high thermal conductivity<sup>(39)</sup>. The thermal conductivity of single crystals of AlN along the c-axis has been measured from 94.4°K to 1843°K and is shown in Figure 11. The crystals were grown by sublimation in sealed tungsten crucibles. The data from 94.4°K to 307°K were measured on boule W-154 using a steady-state longitudinal-bar heat-flow apparatus with a surrounding radiation shield<sup>(40)</sup>.

The temperatures were measured with chromel-alumel thermocouples. The sample was 1.4cm long and 0.52cm in diameter. The thermocouples were cemented directly to the sample with epoxy resin. The data from 357°K to 1843°K were measured with a laser flash unit<sup>(40)</sup> by R. Tanzilli<sup>(41)</sup> on crystals from W-154 and W-167. The data obtained were values of the thermal diffusivity, and these were converted to thermal conductivity using the specific heat capacity.

Figure 11 also gives the high temperature thermal conductivity data of Sakai et al.<sup>(42)</sup> and Fridlender et al.<sup>(43)</sup> on AlN with <0.1 wt% oxygen. The present material from run W-154 probably has <0.05 weight % oxygen. The effect of oxygen on the thermal conductivity of AlN has been discussed by Slack<sup>(39)</sup>. Note that the data of Sakai et al. with a considerable oxygen content is considerably below the present results for low oxygen content material. The thermal conductivity of SiC is also given<sup>(39)</sup> in Figure 11 to demonstrate that SiC and AlN, when pure, behave in a very similar manner.

The Debye temperature<sup>(39)</sup> of AlN is 950°K. Above 950°K the thermal conductivity,  $K$ , varies very nearly as  $T^{-1}$ . At 300°K it varies as  $T^{-2.0}$ , while at 100°K it varies as  $T^{-2.2}$ . Since Al is isotopically pure and N is 99.6% of  $N^{14}$ , the isotope scattering at temperatures below 100°K should be very small<sup>(44)</sup>. Thus in a pure crystal the  $K$  at low temperatures should rise exponentially with decreasing temperature. The best values for the intrinsic  $K$  of AlN versus  $T$  are given in Table III. Note that at room temperature the value is 2.9 watt/cm deg., which is 73% of that of copper. Thus pure AlN is really an excellent material for heat sinks.

## Section 3

## RECOMMENDATIONS FOR FUTURE WORK

1. A better method is needed for preparing AlN of high purity in a dense, low-surface-area form with no oxygen contamination. The aluminum metal-organic route looks promising and should be tried.
2. A little more effort on the liquid droplet method is needed in order to obtain small droplets about 1mm in diameter consistently.
3. Further study of the sublimation/growth rates of AlN in  $N_2$  plus  $H_2$  mixtures at pressures above 1 atmosphere is needed. If the predictions are accurate then polycrystalline tungsten crucibles can be used for growing crystals.
4. Data on the elastic constants and piezoelectric constants are needed on the crystals now in hand.

TABLE I: Dissociation Energies of  
Various Gaseous Molecules

	0°K (Electron Volts)	2600°K (Electron Volts)
$1/2 \text{ N}_2 \rightarrow \text{N}$	4.88	4.99
$1/2 \text{ H}_2 \rightarrow \text{H}$	2.24	2.37
$\text{NH} \rightarrow \text{N}+\text{H}$	3.61	3.84
$\text{NH}_2 \rightarrow \text{N}+\text{H}+\text{H}$	7.59	8.06
$\text{NH}_2 \rightarrow \text{N}+\text{H}_2$	3.11	3.32
$\text{NH}_3 \rightarrow \text{N}+\text{H}+\text{H}+\text{H}$	12.00	12.65
$\text{NH}_3 \rightarrow \text{N}+\text{H}+\text{H}_2$	7.52	7.91
$\text{AlN(s)} \rightarrow \text{Al(s)} + \text{N(g)}$	8.124	7.85

TABLE II: Melting and Boiling Points of Some Useful Compounds

Compound	M.P. °C	B.P. °C	Name
Me <sub>3</sub> Al	+13	+126	Trimethyl aluminum
Et <sub>3</sub> Al	-53	+186	Triethyl aluminum
NH <sub>3</sub>	-78	-33	Ammonia
NH <sub>2</sub> Me	-93	-7	Methyl amine
NH <sub>2</sub> Et	-81	+16	Ethyl amine
Me <sub>3</sub> Al·NH <sub>3</sub>	+57		Trimethyl aluminum-ammonia
Et <sub>3</sub> Al·NH <sub>3</sub>	< 0		Triethyl aluminum-ammonia
Me <sub>3</sub> Al·NH <sub>2</sub> Me	+56		Trimethyl aluminum methyl amide
Me <sub>2</sub> Al·NH <sub>2</sub>	+134		Dimethyl aluminum amide
Et <sub>2</sub> Al·NH <sub>2</sub>	-57		Diethyl aluminum amide
Me <sub>2</sub> Al·NH Me	+110		Dimethyl aluminum-methyl amide
MeAl·NH	?		Methyl aluminum imide
EtAl·NH	?		Ethyl aluminum imide
C <sub>6</sub> H <sub>6</sub>	+6	+80	Benzene
C <sub>12</sub> H <sub>6</sub>	+7	+81	Cyclohexane
Ch <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	-95	+110	Toulene

Me = methyl = -CH<sub>3</sub>, Et = ethyl = -C<sub>2</sub>H<sub>5</sub>

TABLE III: Intrinsic Thermal Conductivity of AlN  
as a Function of Temperature

<u>K</u> Watt/cm deg	<u>T</u> °K	<u>K</u> Watt/cm deg	<u>T</u> °K
28	100	0.83	600
11.5	150	0.56	800
6.4	200	0.42	1000
2.9	300	0.27	1500
1.6	400	0.20	2000
1.10	500	0.13	3000

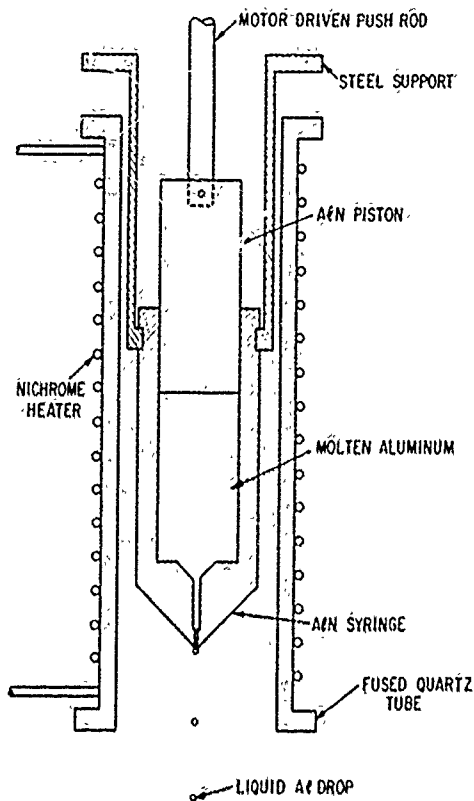
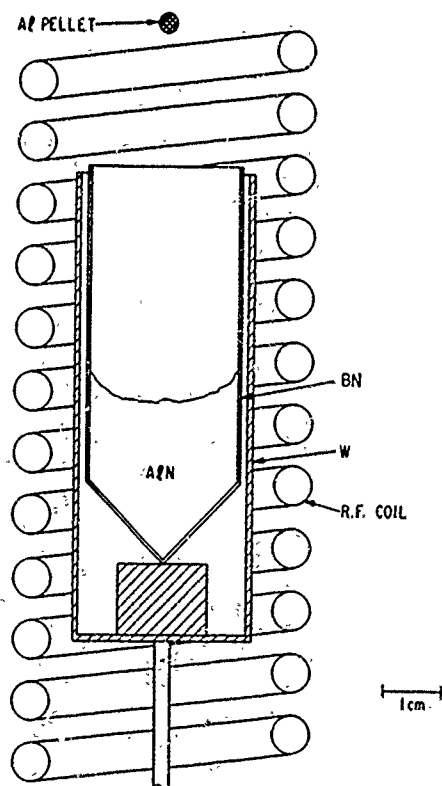


Figure 1. Motor Driven Syringe for Producing Small Droplets of Liquid Aluminum. Operating temperature is about 800°C.

Figure 2. R.F. Heated Tungsten Susceptor and Pyrolytic Boron Nitride Crucible for Catching the Aluminum Droplets. Operating temperature is about 1800°C.





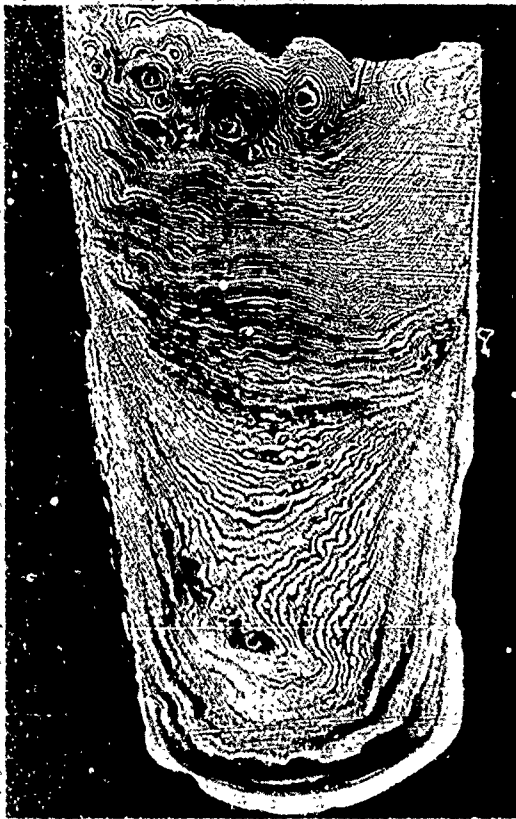


Figure 3. Cross-section of AlN Charge Made in Run W252 Using the Aluminum Syringe and a  $0.95\text{N}_2 + 0.05\text{H}_2$  Atmosphere. The charge diameter is 19 mm at the top.

Figure 4. Cross-Section of AlN Charge Made in Run W250 Using the Aluminum Syringe and a  $0.25\text{N}_2 + 0.75\text{H}_2$  Atmosphere. The charge diameter is 8.6 mm at the top.



Figure 5. The Sublimation Rate of AlN From an Exposed Surface Into a Sink at Absolute Zero as a Function of the Surface Temperature. The  $N_2 + 3H_2$  come from thermally decomposed  $NH_3$ . The points refer to individual runs of 1 to 10 hours duration.

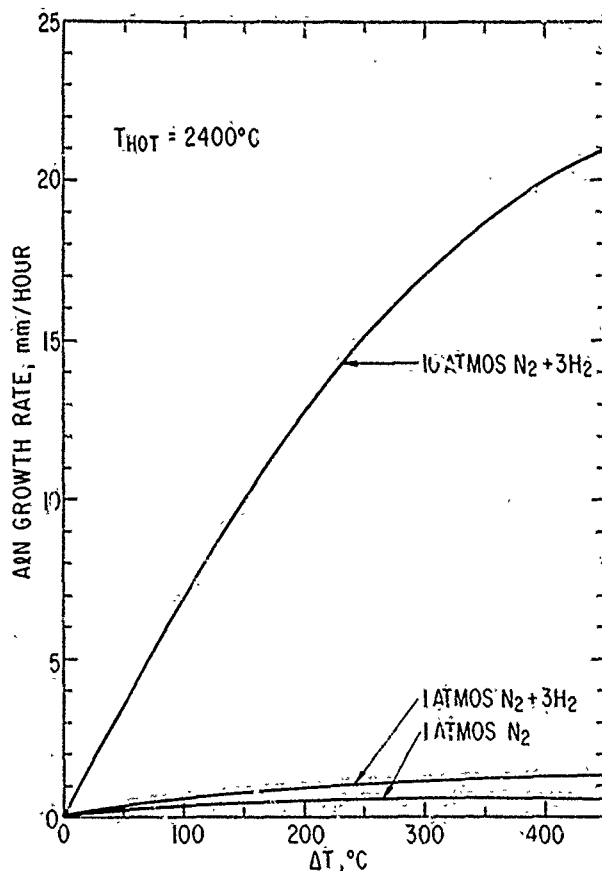
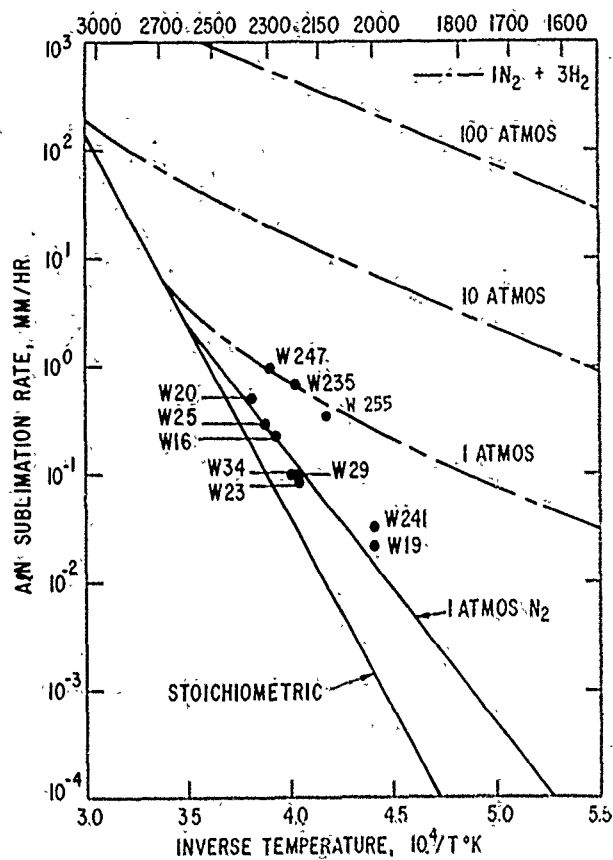


Figure 6. The Growth Rate of AlN Crystals in a Two-Zone Crucible as a Function of the Hot-Cold Temperature Difference and the Gas Atmosphere. The hot end is held at  $2400^\circ C$ .



Figure 7. Photograph of a Tungsten Crucible and Cap Made from a Single Crystal of Tungsten. The crucible is 7.1 cm long.

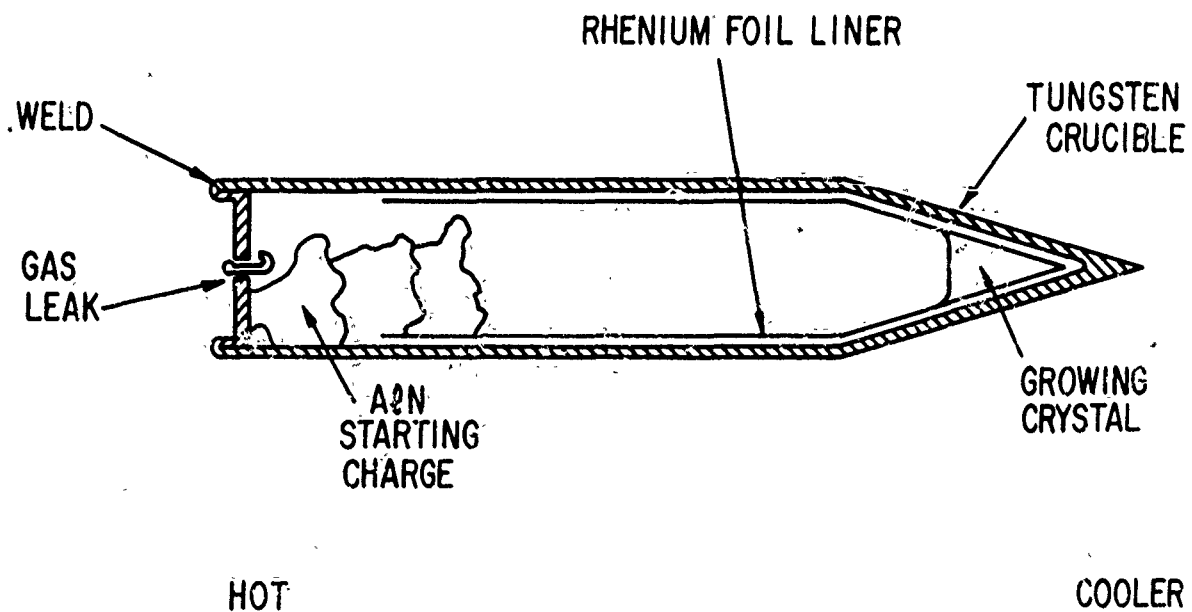


Figure 8. Schematic of Single Crystal Tungsten Crucible with Rhenium Liner and AlN Inside.

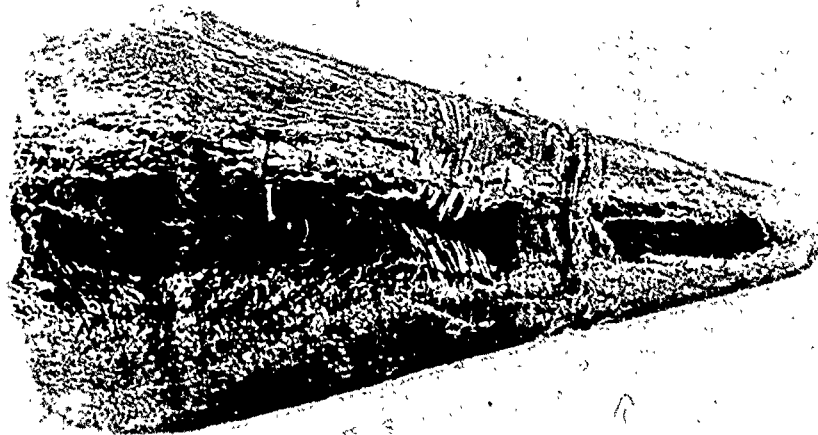


Figure 9. Photograph of a Single Crystal of AlN W253 Grown in the Crucible in Figure 8, Side View. The scale divisions are millimeters.

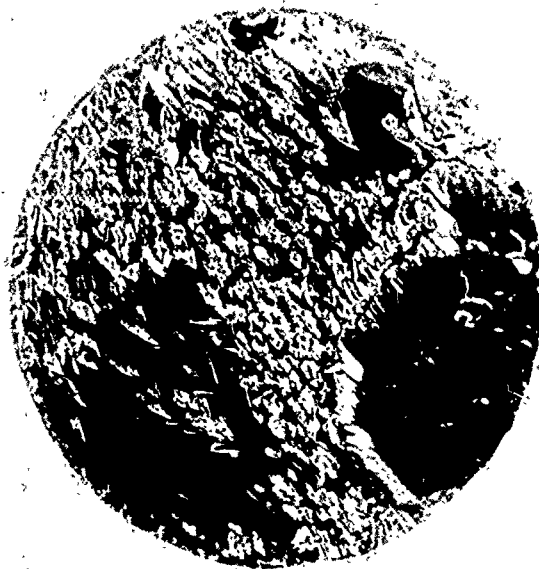


Figure 10. Photograph of Top of AlN Crystal W253. The crystal diameter is 9 mm.

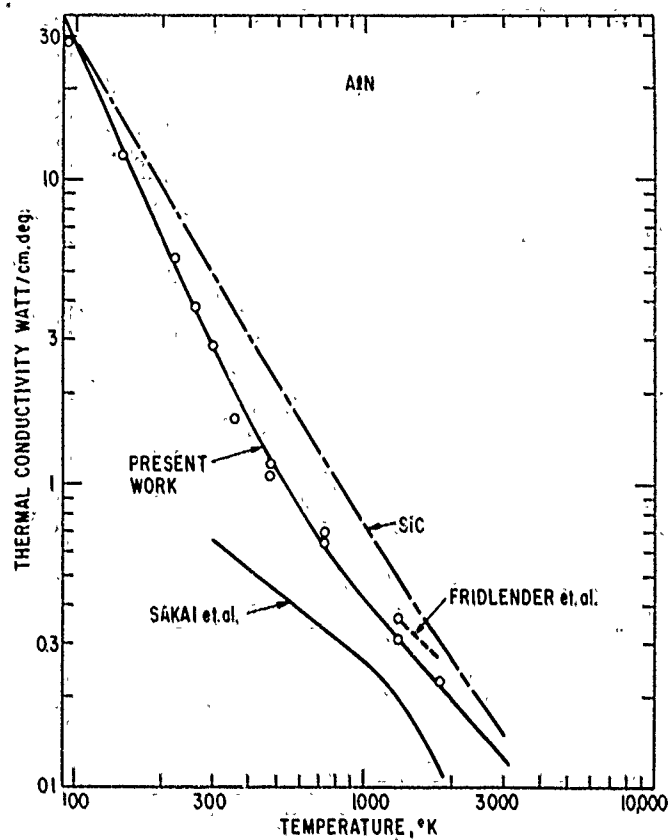


Figure 11. The Thermal Conductivity of Single Crystal AlN Along the C-Axis as a Function of Temperature.

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